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TITLE: PRODUCTION OF POLYMER ENCAPSULATED  
IN MICROCAPSULE

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ABSTRACT:

PROBLEM TO BE SOLVED: To obtain the subject spherical polymer having a smooth flat surface without having a coating by containing a polymerization suppressor in an aqueous phase.

SOLUTION: This method for producing a polymer encapsulated in microcapsules, is constituted by containing 10-1000ppm polymerization suppressing agent in a water phase based on the total amount of the aqueous phase and the

polymerization suppreessor, and polymerizing monomer droplets contained in microcapsule (suspended in the aqueous phase) and containing a crosslinking agent and an initiator at 50-150&deg;C. As the polymerization suppressor, an inorganic compound selected from a nitrogen compound, a salt of phosphoric acid, a compound containing sulfur and a peroxide (e.g.; hydroxylamine) or an organic compound selected from a phenolic compound, a nitrogen compound, an unsaturated lactone, a hydroxyketone and a compound containing sulfur (e.g.; N, N-diethylhydroxylamine) are preferable. As the monomer, styrene (mixture) is preferable. A cation exchanging material can be obtained by e.g. sulfonating the obtained polymer and imparting a functional group.

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture method of the polymer enclosed with the microcapsule by the polymerization of the monomer drop contained in a microcapsule (it suspended in the aqueous phase) characterized by an aqueous phase containing at least one sort of polymerization retarders.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of the polymer enclosed with the microcapsule by the polymerization of the monomer enclosed with the microcapsule.

[0002]

[Background of the Invention] Since the ion exchanger with the most uniform possible particle size (henceforth "uniform dispersibility (monodisperse)") offers an advantage with the more suitable economical hydrodynamic property of the exchanger bed of a uniform dispersibility ion exchanger in many uses, the importance has increased recently. A uniform dispersibility ion exchanger can be manufactured by giving a functional group to uniform dispersibility bead polymer. One of the possibility for manufacturing uniform dispersibility bead polymer is spraying a monomer into a continuous phase, manufacturing a uniform dispersibility monomer drop, and hardening these by the polymerization subsequently. Generation of the particle size of a uniform drop may be supported by oscillating stimulus. That is, the manufacture method of the globular form monomer drop with a uniform particle size by carrying out the oscillating stimulus of the monomer of a laminar flow is indicated by the Europe patent No. 51210 specification. When the uniform dispersibility of a monomer drop must be held between polymerizations, condensation and reforming of a drop must be eliminated. In order to prevent condensation and reforming of a drop, especially an effective method includes enclosure to the microcapsule of the drop by the Europe patent No. 46535 specification.

[0003]

[Problem(s) to be Solved by the Invention]

[0004]

[Means for Solving the Problem] Even if it carried out the polymerization of the monomer drop enclosed with the microcapsule, the bead polymer with a smooth front face was not necessarily generated, namely, it was found out coarsely that bead polymer with/ or the covered front face can generate. Since in the case of many uses especially surface coating is removed by after treatment, or it is removed with a capsule wall while giving a functional group to bead polymer and obtaining an ion exchanger, surface granularity or surface surface coating does not serve as a fault. However, in order to use bead polymer as a seed in the case of some uses, for example, the so-called so-called kind / supply process, bead polymer with a smooth front face is desired. "A kind / supply process (seed/feed process)" expands in the monomer which can copolymerize polymer, and this monomer carries out the polymerization of it, and it is understood to be what means the method by which the expanded polymer particle is generated.

[0005] Being formed between the polymerizations of the monomer by which the globular form polymer with a good front face (that is, there is no covering and it has a smooth front face) was enclosed with the microcapsule suspended in the water phase when a monomer and/ or a water phase contained at least one sort of polymerization retarders was found out this time.

[0006] Therefore, this invention relates to the manufacture method of the polymer enclosed with the microcapsule by the polymerization of the monomer drop contained in a microcapsule (it suspended in the water phase) characterized by a water phase containing at least one sort of polymerization retarders. Besides a monomer, a monomer drop contains a cross linking agent again.

[0007] The polymer enclosed with the microcapsule manufactured according to this invention is direct, or is converted into an ion exchanger by grant of a functional group through the intermediate-stage story of the polymer particle expanded according to sowing / supply process again.

[0008] It is understood that a "monomer" means a compound with the C=C double bond in which styrene, vinyltoluene, ethyl styrene, an alpha methyl styrene, chloro styrene, a chloro methyl styrene, an acrylic acid, a methacrylic acid, an acrylic ester, a methacrylic ester, acrylonitrile, a methacrylonitrile, an acrylamide, methacrylamide, and one polymerization like the mixture of these compounds are possible.

[0009] The mixture of styrene and styrene, and the above-mentioned monomer is suitable.

[0010] The cross linking agents which can be used are at least two compounds which have suitably the C=C double bond in which two or three polymerizations are possible. As a suitable cross linking agent, they are a divinylbenzene, divinyl toluene, trivinylbenzene, divinyl naphthalene, TORIBI nil naphthalene, the diethylene-glycol divinyl ether, 1, 7-OKUTA diene, 1, 5-hexadiene, ethylene-dimethacrylate glucosol, a methacrylic acid triethylene glycol, a TORIMETA krill acid trimethyl propane, a methacrylic-acid allyl compound, and a methylene. - An N and N'-screw acrylamide is mentioned. The property of



a cross linking agent can be chosen from the point of use of the after that of polymer. Since ester combination is decomposed under sulfonation conditions when it follows, for example, a cation exchanger must be manufactured according to sulfonation from polymer, an acrylic ester or a methacrylic-ester cross linking agent is seldom suitable. In many cases, in manufacture of a strong acid nature cation exchanger, especially the divinylbenzene is suitable. In the case of most many uses, the divinylbenzene grade of marketing also containing an ethyl vinylbenzene is suitable out of the isomer of a divinylbenzene. a cross linking agent -- general -- the whole quantity of a monomer and a cross linking agent -- being based -- 0.05-10 -- suitable -- 0.1-5 -- it is especially used in 0.1 - 1% of the weight of an amount suitably The monomer should be \*\*\*\* insolubility in the water phase. So, the monomer which is fusibility in part in underwater [ like an acrylic acid, a methacrylic acid, and acrylonitrile ] is suitably used as mixture with a water-insoluble nature monomer. It is also possible to decrease the solubility of the monomer in the inside of a water phase by addition of a salt.

[0011] The possible matter for enclosing a monomer drop with a microcapsule is the thing known for this purpose especially polyester, natural and synthetic poly AMINO, polyurethane, and the poly urea. Especially gelatin is suitable as a natural polyamide. Especially this is used as a coacervate and a compound coacervate. The gelatin content compound coacervate in the context of this invention divides, and is understood to mean the combination of gelatin and a synthetic-macromolecule electrolyte. A suitable synthetic-macromolecule electrolyte is a copolymer with the mixed unit of a maleic acid, an acrylic acid, a methacrylic acid, an acrylamide, and methacrylamide. In a usual adjuvant like formaldehyde or a guru taro dialdehyde, a gelatin content capsule wall is hardened and can carry out things. The gelatin content capsule matter is suitable in the context of this invention.

[0012] Enclosure to the capsule of the monomer drop by gelatin, the gelatin content coacervate, and the gelatin content compound coacervate is indicated in detail by for example, the Europe patent No. 46535 specification. The encapsulation method by synthetic polymer is known in itself. The second reactant component (for example, amine) which dissolved the reactant component (for example, isocyanate or an acid chloride) which dissolved into the monomer drop into the water phase, and especially the boundary condensation to which it is made to react are suitable for this.

[0013] The monomer enclosed by the capsule out of a cross linking agent contains the initiator for starting a polymerization again. The initiator suitable for the method by this invention For example, dibenzoyl peroxide, A dilauryl peri oxide, screw - (p-chloro benzoyl peroxide), Carboxylic-acid dicyclohexyl pel OKISHIJI, pel OKUTO acid t-butyl, 2, 5-screw - (2-ethyl HIKISA noil peroxy) A peroxy compound like -2, 5-dimethyl hexane, and a t-amyl peroxy-1-ethyl-hexane, And it is an azo compound like further 2, 2'-azobis - (isobutyronitrile), and 22'-azobis - (2-methyl isobutyronitrile). an initiator -- general -- the whole quantity of a monomer and a cross linking agent -- being based -- 0.05-2.5 -- it is suitably used in 0.1 - 1.5% of the weight of an amount

[0014] The monomer enclosed with a capsule contains the so-called polo gene (porogen) which generates fine porosity structure in polymer again. The organic solvent which the generated polymer seldom dissolves or swells is suitable for this. The examples which may be indicated are a hexane, an octane, an isooctane, an iso dodecane, a methyl ethyl ketone, and an octanol.

[0015] The monomer contained in a capsule contains the bridging polymer or non-bridging polymer to 30 % of the weight again based on the matter enclosed with a capsule. them of the monomer of the above [ suitable polymer ] -- they are them of styrene especially suitably

[0016] The mean particle diameters of the monomer drop enclosed with the capsule are 10-1000, especially 100-1000 micrometers suitably. The method by this invention is suitable for manufacture of uniform dispersibility polymer, especially the Europe patent No. 46535 specification at them of a publication.

[0017] The polymerization retarders in this invention are whether the free radical polymerization of a compound with the C=C double bond in which a polymerization is possible is delayed, and matter suppressed completely.

[0018] The polymerization retarder used according to this invention can be inorganic or an organic substance. As a suitable inorganic inhibitor, salt of hydrazine, hydroxylamine, nitro compound, for example, Fremy salt (oximido disulfonic-acid potassium); nitrite, for example, sodium nitrite, and potassium-nitrite; phosphorous acid, for example, phosphorous acid hydrogen sodium; sulfur content compound, for example, sodium dithionite, sodium-thiosulfate, sodium-sulfite, sodium-bisulfite, sodium-thiocyanate, and ammonium-thiocyanate; and a peroxy compound, for example, a hydrogen peroxide, a sodium perborate, or a fault sodium carbonate is mentioned.

[0019] As a suitable organic inhibitor, a hydroxy aromatic compound, for example, a hydroquinone, The hydroquinone monomethyl ether, a resorcinol, a pyrocatechol, The condensation product of t-butyl pyrocatechol, pyrogallol, p-nitrosophenol and a phenol, and an aldehyde; A nitrogen content compound, For example, N and N-diethylhydroxylamine, A hydroxylamine derivative like N-isopropyl hydroxylamine and sulfonation, or carboxylation N-alkyl hydroxylamine or N, and N-dialkyl hydroxylamine derivative; A hydrazine derivative, Further again For example, N and N-hydrazino 2 acetic acid; And a nitroso compound, For example, N-oximido phenyl hydroxylamine, N-oximido phenyl-hydroxylamine ammonium salt, or N-oximido phenyl-hydroxylamine aluminum salt; Unsaturation lactone, For example, an ascorbic acid, a sodium ascorbate, isoascorbic acid, and iso ASUKORIBIN acid sodium; hydroxyketone, for example, dihydroxyacetone,; and a sulfur content compound, for example, a sodium isopropylxanthate, are mentioned.

[0020] If the polymerization retarder which is used according to this invention in many cases was fusibility in the water phase, it turns out that it is advantageous. The "fusibility" in this point means that it can dissolve without at least 1000 ppm's leaving a residue in a water phase at 70 degrees C. This is influenced in many cases by suitable selection of conditions, for example, the solubility of a phenol nature inhibitor can improve with high pH. The amount of a polymerization retarder is chosen so

that the polymerization of the monomer in the outside of a capsule wall or a monomer, and a cross linking agent may be prevented. Out of being dependent on the amount of the polymerization retarder used, the initial complement of a polymerization retarder is greatly dependent on the solubility of the inhibitor in the inside of inhibitor activity and a water phase again. Several experiments can determine the optimal amount easily. Although the inhibitor content of a commercial cross linking agent is generally 0.001 - 0.01 % of the weight based on a cross linking agent, it is inadequate for the purpose of this invention. However, it becomes together with the inhibitor added additionally, and it contributes to a desired effect. the usual amount of a polymerization retarder -- the whole quantity (water phase + inhibitor) -- being based -- 10-1000 -- suitable -- 10-500 -- it is within the limits of 10-250 ppm especially

[0021] A commercial monomer and a commercial cross linking agent can contain an inhibitor because of stabilization. However, since the concentration is very low, the concentration in the water phase which this invention takes is not reached, and the effect by this invention does not happen.

[0022] the polymerization of the drop of the monomer enclosed with the capsule for obtaining globular form polymer -- convenient -- one sort or the protective colloid beyond it -- it can carry out under existence of the buffer system in a water phase appropriately As protective colloid, a copolymer with natural and synthetic - water-soluble polymer, for example, gelatin, starch, polyvinyl alcohol, polyvinyl PIROPIDON, a polyacrylic acid, a polymethacrylic acid, an acrylic acid, and (meta) an acrylic ester is mentioned. A cellulosic especially a cellulose ester and a cellulose ether, for example, a carboxymethyl cellulose, a methyl hydroxyethyl cellulose, methyl hydroxypropylcellulose, and the hydroxyethyl cellulose are also especially suitable. Gelatin is suitable especially as protective colloid in the case of the polymerization of the monomer drop enclosed with the capsule by gelatin and the gelatin content compound coacervate. the amount of the protective colloid used -- general -- a water phase -- being based -- 0.025-1.5 -- it is 0.05 - 0.75 % of the weight suitably

[0023] A polymerization can be performed under existence of a buffer system. At the time of the start of a polymerization, 14-6, and the buffer system suitably adjusted to the value of 12-8 within the limits are suitable in pH of a water phase. the protective colloid which has a carboxylic-acid machine under these conditions -- all -- or it exists as a salt in part An operation of protective colloid is suitably influenced by this method. Especially a suitable buffer system contains phosphate or a borate. The term "phosphate and a borate" in this invention contains the condensation product of the corresponding ortho mold of an acid and a corresponding salt again. The concentration of the phosphate in a water phase or a borate is [ 1. ] 2.5-100mm a mol/l. suitably 0.5-500mm a mol /.

[0024] Unlike usual beads polymerization, the agitating speed under polymerization does not have influence in the particle size of a particle not much importantly. A microcapsule is held in suspension and sufficient low agitating speed to remove the heat of polymerization is used.

[0025] the volume ratio to the water phase of the monomer drop enclosed with the capsule -- general -- 1:0.75-1:20 -- it is 1:1-1:6 suitably

[0026] It depends for polymerization temperature on the dissociation temperature of the initiator used. Generally it is 55-100 degrees C suitably 50-150 degrees C. A polymerization continues from 0.5 for several hours. It turns out that it is appropriate to use the temperature program which reaction temperature increases as polymerization conversion advances by leaving at temperature with a low polymerization, for example, 60 degrees C. The high-reliability process of a reaction and the requirements for high polymerization conversion are especially satisfied good by this. After a polymerization, polymer can be isolated by the usual method, for example, filtration, or the decantation, and can be appropriately dried after washing beyond 1 time or it.

[0027] The matter of a capsule wall is on the front face of bead polymer substantially. According to a request, this matter is removable with after treatment. Gelatin and a gelatin content compound coacervate are easily washed with an acid or alkali, and can do last thing.

[0028] However, since the capsule wall matter is removed under the conditions which give a functional group to polymer and obtain an ion exchanger by any case in many cases, the capsule wall matter is washed and last thing is not required.

[0029] The data of the percent of the following examples are based on each \*\*\*\* weight.

[0030]

[Example]

Example 1 There is no surface coating and 1580ml deionized water is introduced into the manufacture beginning of the polymer enclosed with the microcapsule into a 4l. glass reactor. It consisted of a divinylbenzene (commercial divinylbenzene isomer mixture of 63% purity in ethyl styrene), 0.75% dibenzoyl peroxide, and 98.45% styrene 0.8%, and 790g of mixture enclosed with the microcapsule was added. A microcapsule consists of gelatin and an acrylamide / an acrylic-acid copolymer, and contains the compound coacervate hardened with formaldehyde. A mean particle diameter is 231 micrometers. The solution (the 2.4g gelatin in 80ml deionized water, phosphoric-acid hydrogen sodium 12 4g hydrate, and 410mg) of N and N-diethylhydroxylamine (83% purity) is added into mixture, agitating mixture slowly and agitating it, temperature is raised and a polymerization is completed. By 32-micrometer plus sieve, mixture is washed and it dries. The polymer enclosed with the microcapsule with a 760g smooth front face of a non-globular form is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.

[0031] Example 2 Although the manufacture experiment of the polymer enclosed with the microcapsule which does not have surface coating and does not have covering is conducted like an example 1, 100mg N and N-diethylhydroxylamine (83% purity) is used. It has a 760g globular form and a smooth front face, and the polymer enclosed with the microcapsule is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.



[0032] Example 3 There is no surface coating, and although the manufacture experiment of the polymer enclosed with the microcapsule is conducted like an example 1, 60mg N and N-diethylhydroxylamine (85% purity) is used. It has a 760g smooth front face, and the polymer enclosed with the globular form microcapsule is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.

[0033] Example 4 It has slight surface coating, and although the manufacture experiment of the polymer enclosed with the microcapsule is conducted like an example 1, 30mg N and N-diethylhydroxylamine (85% purity) is used. It has the surface coating of 760g a few, and the polymer enclosed with the globular form microcapsule is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.

[0034] Example 5 Manufacture of the polymer which has much surface coating and was enclosed with the microcapsule (comparison)

N and N-diethylhydroxylamine is not used although an experiment is conducted like an example 1. It has the covered 760g front face, and the polymer enclosed with the globular form microcapsule is obtained. Polymer looks [ be / white / it ] optical and a mean particle diameter is 220 micrometers.

[0035] Example 6 It has surface coating, and although the manufacture experiment of the polymer enclosed with the microcapsule is conducted like an example 1, a 700mg hydroxylamine is used instead of N and N-diethylhydroxylamine (50% purity). It has a 760g smooth front face, and the polymer enclosed with the globular form microcapsule is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.

[0036] Example 7 There is no surface coating, and although the manufacture experiment of the polymer enclosed with the microcapsule is conducted like an example 1, a 350mg resorcinol is used instead of N and N-diethylhydroxylamine. It has a 760g smooth front face, and the polymer enclosed with the globular form microcapsule is obtained. Polymer looks [ be / transparent / it ] optical and a mean particle diameter is 220 micrometers.

[0037] In addition, the main feature and main mode of this invention are indicated below.

[0038] 1. Manufacture method of polymer enclosed into microcapsule (it suspended in water phase) by microcapsule by polymerization of content rare \*\* monomer drop characterized by water phase containing at least one sort of polymerization retarders.

[0039] 2. Method given in claim 1 in which monomer drop contains styrene and cross linking agent.

[0040] 3. Method given in claim 1 whose polymerization retarder is inorganic compound.

[0041] 4. Method given in claim 3 chosen from group which polymerization retarder becomes from nitride, salt of phosphoric acid, sulfur content compound, and peroxy compound.

[0042] 5. Method given in claim 1 whose polymerization retarder is organic compound.

[0043] 6. Method given in claim 5 chosen from group which polymerization retarder becomes from phenol nature compound, nitride, unsaturation lactone, hydroxyketone, and sulfur content compound.

[0044] 7. Method given in claim 1 whose amount of polymerization retarder is 10-1000 ppm based on the total quantity of aqueous phase and inhibitor.

[0045] 8. Manufacture method of ion exchanger by giving functional group to product obtained by claims 1-7 by method of publication.

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[Translation done.]